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14. ABSTRACT
Two-dimensional (2D) crystalline atomic sheets are currently a topic of widespread investigation. They are a platform to investigate new paradigms in material science, solid-state physics, and field-effect phenomena that can enable future generations of energy, computation, and sensor technologies. This report summarizes the results of this effort on focusing on rare-earth arsenides (RE-A), although not a van der Waals 2D solid, nonetheless, exhibits substantial 2D quantum size effects. In addition, unlike van der Waals 2D solids, the RE-A can be synthesized by

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Report Title

Final Report: Materials Science--10.4. Physical Properties of Materials: "Supported and Free-Standing 2D Semimetals"

ABSTRACT

Two-dimensional (2D) crystalline atomic sheets are currently a topic of widespread investigation. They are a platform to investigate new paradigms in material science, solid-state physics, and field-effect phenomena that can enable future generations of energy, computation, and sensor technologies. This report summarizes the results of this effort on focusing on rare-earth arsenides (RE-A), although not a van der Waals 2D solid, nonetheless, exhibits substantial 2D quantum size effects. In addition, unlike van der Waals 2D solids, the RE-A can be synthesized by molecular beam epitaxy (MBE) on standard III-V substrates, and the presence of dangling bond surfaces can provide a degree of freedom to further control material properties.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/15/2015	6.00	E. M. Krivoy, S. Rahimi, H. P. Nair, R. Salas, S. J. Maddox, D. J. Ironside, Y. Jiang, V. D. Dasika, D. A. Ferrer, G. Kelp, G. Shvets, D. Akinwande, S. R. Bank. Growth and characterization of single crystal rocksalt LaAs using LuAs barrier layers, Applied Physics Letters, (11 2012): 101. doi: 10.1063/1.4766945
08/29/2013	4.00	S. Rahimi, E. M. Krivoy, J. Lee, M. E. Michael, S. R. Bank, D. Akinwande. Temperature dependence of the electrical resistivity of LaxLu1-xAs, AIP Advances, (08 2013): 0. doi: 10.1063/1.4817830
08/29/2013	5.00	E. M. Krivoy, H. P. Nair, A. M. Crook, S. Rahimi, S. J. Maddox, R. Salas, D. A. Ferrer, V. D. Dasika, D. Akinwande, S. R. Bank. Growth and characterization of LuAs films and nanostructures, Applied Physics Letters, (10 2012): 0. doi: 10.1063/1.4757605

TOTAL: **3**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
01/15/2015	7.00	E.S. Walker, , E. Krivoy, , M. Yogeesh, , D. Akinwande, , S.R. Bank. Semiconducting Bismuth Thin Films Grown by Molecular Beam Epitaxy for Device Applications, Electronic Materials Conference. 26-JUN-14, . : ,
TOTAL:		**1**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
08/30/2012	1.00	Jong H. Lee, Domingo A. Ferrer, Deji Akinwande, Seth R. Bank, Adam M. Crook, Hari P. Nair. Growth of semimetallic ErAs films epitaxially embedded in GaAs, Nanoepitaxy: Materials and Devices III. , San Diego, California, USA. : ,
TOTAL:		**1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
08/30/2012	2.00	S. Rahimi, E.M. Krivoy, J. Lee, M.E. Michael, S. R. Bank, D. Akinwande. Temperature dependent electrical resistivity and resistivity tuning of LuAs thin films by Lanthanum , Applied Physics Letters (to be submitted) (09 2012)
08/30/2012	3.00	E.M. Krivoy, S. Rahimi, H.P. Nair, S.J. Maddox, R. Salas, Y. Jiang, M.A. Belkin, D. Akinwande, S.R. Bank. Growth and characterization of single crystal rocksalt LaAs using LuAs barrier layers, Applied Physics Letters (under consideration) (08 2012)

TOTAL: **2**

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Jack Kilby Faculty Fellowship

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
graduate student	0.50	
FTE Equivalent:	**0.50**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Deji Akinwande	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Technology transfer between my lab and ARL scientists are underway, focusing on joint effort to better understand the properties of the 2D materials and how it can benefit Army science.

Supported and Free-Standing 2D Semimetals

PI: Deji Akinwande, The University of Texas – Austin, TX

Two-dimensional (2D) crystalline atomic sheets are currently a topic of widespread investigation. They are a platform to investigate new paradigms in material science, solid-state physics, and field-effect phenomena that can enable future generations of energy, computation, and sensor technologies. This report summarizes the results of this effort on focusing on rare-earth arsenides (RE-A), although not a van der Waals 2D solid, nonetheless, exhibits substantial 2D quantum size effects. In addition, unlike van der Waals 2D solids, the RE-A can be synthesized by molecular beam epitaxy (MBE) on standard III-V substrates, and the presence of dangling bond surfaces can provide a degree of freedom to further control material properties. They are known to be semimetallic in the bulk phase owing to a small overlap of the conduction and valence bands quite similar to the case of graphite. For nanoscale thickness they can become semiconducting. The experimental study led to several new results including:

i- MBE growth of ErAs consisting of a few monolayers. Conductivity studies indicated strong dimensional effects in the solid-state properties such as three orders of magnitude reduction in the conductivity of 3ML compared to bulk ErAs films (Fig. 1). In addition, field-effect transistor phenomena was observed albeit weak for the current samples.

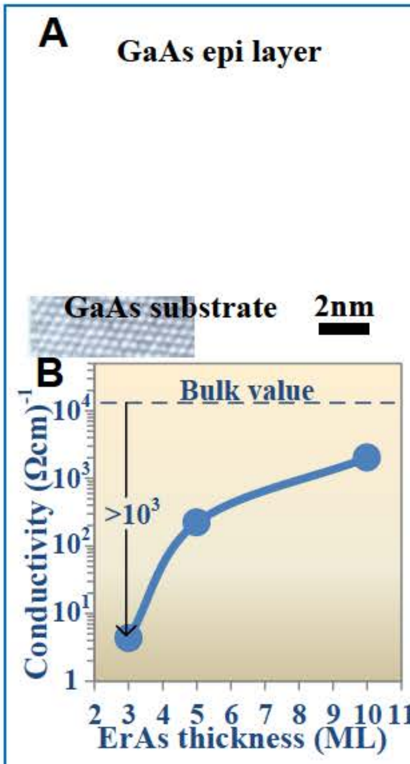

Fig.1 A. Cross-sectional TEM image of recent growth results. **B**. Size effect in the conductivity of ErAs thin films.

ii- First transport studies of LaAs thin films down to 6K confirmed its semimetallic character. Thickness dependent measurements provide an encouraging indication for the potential for strong dimensional effects that might lift the band overlap and result in a small bandgap semiconductor similar to graphene. The epitaxial growth of LaAs was made possible by employing LuAs spacer layers during the MBE growth to prevent intermixing of LaAs and the GaAs substrate. This method led to the expected zinc blende phase of LaAs.

iii- First tunable MBE synthesis and transport studies of $La_xLu_{1-x}As$ single-crystal zinc-blende alloy films (Fig. 2). Epitaxy of 10ML films have been realized showing a multitude of interesting properties including tuning of the lattice constant, resistivity, temperature coefficient of resistivity, optical properties and mobility by La content. The resistivities of these films suggest strong semimetallic character and provide further motivation for continued research for the growth of single or few monolayers.

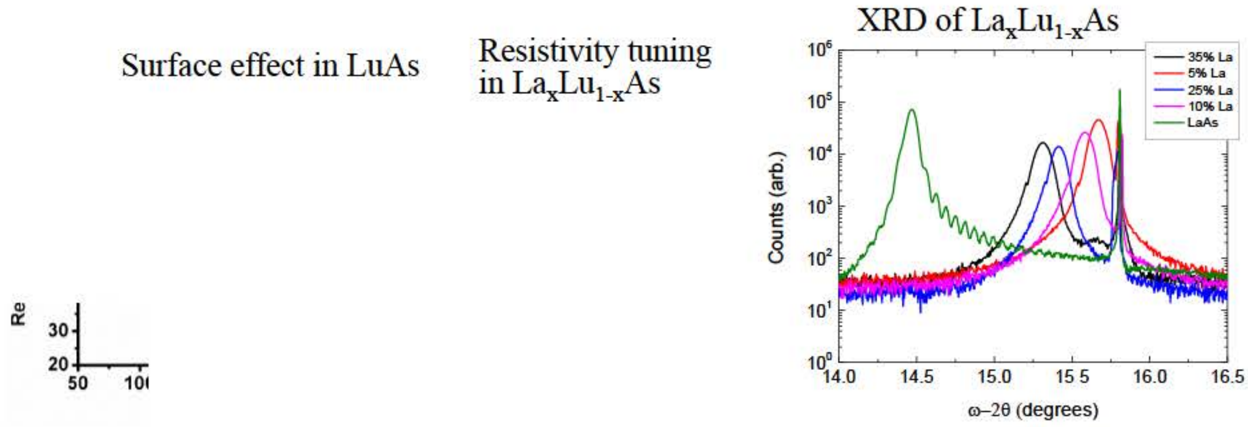

Fig. 2: a) Temperature dependent resistivity of 3 nm and 600 nm LuAs. Resistivity of 3 nm LuAs decreases at a higher rate compared to 600 nm film suggesting scattering of carriers by the interface. b) Resistivity of samples at two end points of the measured temperature range plotted against La concentration. Similar behavior is observed at 78K and 300K. While 15% of La in LuAs increases the resistivity at 300K by 3x, it changes the resistivity at 78K by 4x. c) XRD data of the single-crystal alloy films. The peaks are commensurate with the lattice constant, which is tunable by the La content.

iv- Experimental growth of bismuth, one of the main materials considered in the original ARO proposal. Bismuth is interesting for a variety of reasons including its semimetallic character, anisotropic Fermi surface, low carrier density, vanishingly small effective mass, and long mean free path and Fermi wavelength which results in large quantum or dimensional effects compared to other solid state materials. Our initial attempts to grow Bi on sapphire proved unsuccessful despite the close lattice match. Eventually, we uncovered that low-resistivity Si (111) which has a hexagonal surface is suitable for growing high quality epitaxial bismuth in the (111) orientation. Fig. 3 presents the reflection high-energy electron diffraction (RHEED) images which further confirm the epitaxial growth of 1x1 bismuth. In order to accurately determine the growth rate and further corroborate the material quality, transmission electron microscopy (TEM) was employed for cross-sectional imaging. The images shown in Fig. 4 reveal high structural crystalline quality with no sign of defects on the local scale. Based on the RHEED and TEM data, the growth rate of epitaxial bismuth on Si was estimated to be about 1ML/minute.

Fig. 3: RHEED images confirming the epitaxial growth of bismuth on Si (111) substrate.

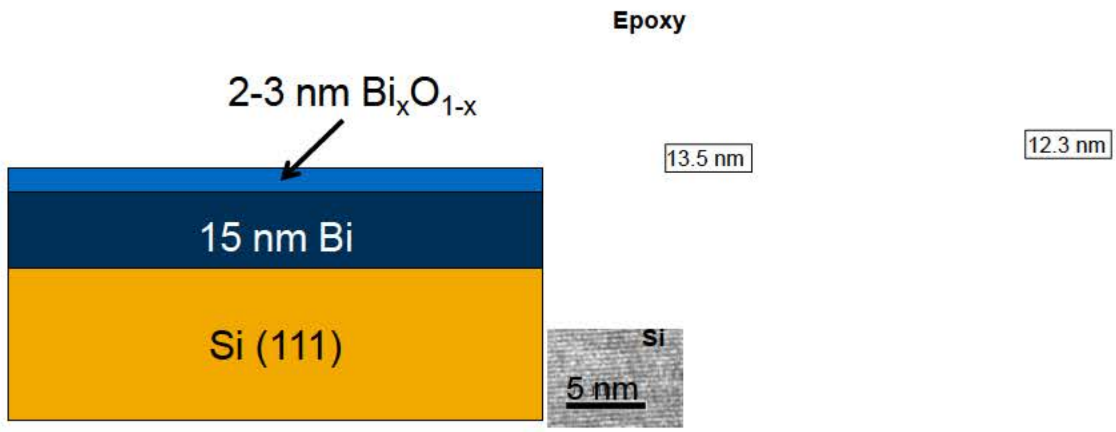

Fig. 4: Cross-sectional schematics of Bi epitaxial growth substrate and capping layer. TEM cross-sectional image of the growth results of ~15nm epitaxial bismuth on silicon substrate. The interface between Bi and Si appear sharp and suggest very little to no intermixing.

This experimental progress has resulted in several publications listed below. Importantly, our pioneering effort on thin bismuth films might provide a route for discovering bismuthene, the van der Waals allotrope of bismuth very similar to its cousin, phosphorene, a puckered 2D crystal. Our future research seeks to uncover the conditions and properties of this previously unexplored nanomaterial, bismuthene.

Publications

i. E.S. Walker, E. Krivoy, M. Yogeesh, D. Akinwande, and S.R. Bank, "Semiconducting Bismuth Thin Films Grown by Molecular Beam Epitaxy for Device Applications," 56th Electronic Materials Conf. (EMC), Santa Barbara, CA, June 2014.

ii. E.M. Krivoy, A. Vasudev, S. Rahimi, R. Synowicki, H.P Nair, D.J. Ironside, G. Kelp, G Shvets, D. Akinwande, M.L. Lee, M. Brongersma and S.R. Bank, "Rare-earth monopnictide alloys for tunable, epitaxial metals" in preparation.

iii. S. Rahimi, E. M. Krivoy, J. Lee, M. E. Michael, S. R. Bank, and D. Akinwande, "Temperature dependence of the electrical resistivity of La[sub x]Lu[sub 1-x]As," AIP Advances, vol. 3, pp. 082102-8, 2013.

iv. S. Rahimi, E. M. Krivoy, J. Lee, M. E. Michael, S. R. Bank, and D. Akinwande, "Temperature and thickness dependence studies of electrical resistivity of LuAs, LaAs, and La[sub x]Lu[sub 1-x]As alloys," in Electronic Materials Conference (EMC), Notre Dame, USA, 2013.

v. J. H. Lee, A. M. Crook, S. R. Bank, and D. Akinwande, "Electric Field-Effect in ErAs Films Embedded in GaAs," in Electronic Materials Conference (EMC), PA, USA, 2012.

vi. E. M. Krivoy, S. Rahimi, H. P. Nair, R. Salas, S. J. Maddox, D. J. Ironside, Y. Jiang, V. D. Dasika, D. A. Ferrer, G. Kelp, G. Shvets, D. Akinwande, and S. R. Bank, "Growth and characterization of single crystal rocksalt LaAs using LuAs barrier layers," Applied Physics Letters, vol. 101, pp. 221908-4, 2012.

vii. E. M. Krivoy, H. P. Nair, A. M. Crook, S. Rahimi, S. J. Maddox, R. Salas, D. A. Ferrer, V. D. Dasika, D. Akinwande, and S. R. Bank, "Growth and characterization of LuAs films and nanostructures," Applied Physics Letters, vol. 101, pp. 141910-4, 2012.

viii. A. M. Crook, H. P. Nair, J. H. Lee, D. A. Ferrer, D. Akinwande, and S. R. Bank, "Growth of semimetallic ErAs films epitaxially embedded in GaAs," in SPIE Proceedings, San Diego, California, USA, 2011, pp. 81060R-7.